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REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION: Unclassified	1b. RESTRICTIVE MARKINGS
AD-A209 123	3. DISTRIBUTION/AVAILABILITY OF REPORT: Approved for public release; distribution unlimited.
	5. MONITORING ORGANIZATION REPORT NUMBER(S): ARO 21767.5-CH
6a. NAME OF PERFORMING ORGANIZATION: University of Missouri	6b. OFFICE SYMBOL (If applicable):
7a. NAME OF MONITORING ORGANIZATION: U. S. Army Research Office	
6c. ADDRESS (City, State, and ZIP Code): Physics Dept., Kansas City MO 64110 Research Reactor, Columbia MO 65211	7b. ADDRESS (City, State, and ZIP Code): P. O. Box 12211 Research Triangle Park, NC 27709-2211
8a. NAME OF FUNDING/SPONSORING ORGANIZATION: U. S. Army Research Office	8b. OFFICE SYMBOL (If applicable):
9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER: DAAG29-85-K-0064	
8c. ADDRESS (City, State, and ZIP Code): P. O. Box 12211 Research Triangle Park, NC 27709-2211	10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification): Structure, Potential Energy Surfaces and Thermodynamic Properties of Hydroxylammonium Nitrate (unclassified)

12. PERSONAL AUTHOR(S): R. D. Murphy and F. K. Ross

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Final	FROM 3/85 TO 1/89	April 1989	7

16. SUPPLEMENTARY NOTATION: The view, opinions and/or findings contained in this report ar ose of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

17. COSATI CODES		
FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number): Hydroxylammonium Nitrate, HAN, X-ray diffraction, neutron diffraction, Monte Carlo

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

In this final report measurements and calculations of the structure of hydroxylammonium nitrate are summarized.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code) / 22c. OFFICE SYMBOL

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ARO 21767.5-CH

STRUCTURE, POTENTIAL ENERGY SURFACES AND THERMODYNAMIC PROPERTIES OF HYDROXYLAMMONIUM NITRATE

FINAL REPORT

R. D. MURPHY and F. K. ROSS

APRIL 1989

U. S. ARMY RESEARCH OFFICE

CONTRACT NO. DAAG29-85-K-0064

UNIVERSITY OF MISSOURI

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STATEMENT OF PROBLEM STUDIED

This is the final technical report on Contract DAAG-29-85-K-0064. The research performed under this contract was primarily designed to produce basic structural information about hydroxylammonium nitrate (HAN), an important ingredient in liquid propellant mixtures under development by the U. S. Army Ballistic Research Laboratory (BRL).

SUMMARY OF MOST IMPORTANT RESULTS

The present contract is an outgrowth of a summer faculty research appointment at BRL in 1983 to one of the principal investigators (Murphy) and a short-term technical assistance (STAS) contract with the other (Ross) in 1984. At the time the proposal (21767-CH) was submitted to ARO, virtually nothing was known of the fundamental properties of HAN and indeed it had not even been crystallized. Due to a large amount of work, much more is now known about HAN. The most important results which we have achieved are as follows:

1) Single pure crystals of HAN were first produced by Ross and subsequently by others at BRL.

2) Both X-ray and neutron diffraction measurements have been made of HAN and/or deuterated HAN. The crystalline structure has been unequivocally determined for a wide range of temperatures and it has been shown that there is only one crystalline phase between 4K and melting (48 °C).

3) The X-ray and neutron diffraction data have been jointly analyzed to display the details of the valence electron distribution in HAN. Electron density maps and form-factor refinement procedures suggest a considerable negative charge on the NH_3OH^+ and less density than expected in the N-O bond. In addition, several NH_3 hydrogen atoms form strong hydrogen bonds to the nitrate group. This suggests a concerted mechanism for decomposition in which NO_3^- is oxidized by transfer of H^+ and the N-O bond is cleaved. Such a mechanism is necessary to explain the intrinsic instability of HAN in the solid state, the liquid and in concentrated solutions.

4) X-ray and neutron liquid scattering experiments have yielded the total structure factor of molten HAN.

5) Theoretical models of the partial structure factors (and from them the total structure) of molten HAN have been made using the Percus-Yevick hard-sphere model. Monte Carlo studies of a number of more complicated models using semi-empirical potentials which are derived from crystalline calculations and which incorporate both the Coulomb interaction and angle-dependent shorter-range potentials have also been done. Agreement is good.

6) As a beginning approach to a perturbation theory of the system, a system of rigid ellipses was studied. A computationally efficient Monte Carlo method was devised to calculate the structure and in principle other properties of this system.

7) Collaborative effort with Dr. Eli Freedman of BRL on intermolecular interactions of nitrogen have continued. This work was begun when Dr. Freedman was Visiting Professor at UMKC and has

led to a substantially better description of the high-temperature virial coefficients of nitrogen. These calculations, which are expected to continue though Dr. Freedman is on emeritus status at BRL, are of importance to BRL's interior ballistics computer codes.

PUBLICATIONS

1. Structure of Hydroxylammonium Nitrate (HAN) and the Deuterium Homolog. A. L. Rheingold, J. T. Cronin, T. B. Brill and F. K. Ross, Acta. Cryst. C43, 402 (1987).

2. Complex Roots of Polynomials by the Newton-Raphson Method. R. D. Murphy, JCMST VII 44 (1987).

3. A Simple Criterion for the Existence of Real Roots of Quartic Equations. Y. J. Wu and R. D. Murphy, Report (1987).

4. Exact Solution of Rate Equations for Consecutive First- and Second-Order Reactions. R. D. Murphy, Report (1987).

5. Monte Carlo Calculations of the Center Pair Distribution Function of a Hard Ellipse System. Y. J. Wu, M.S. Thesis, University of Missouri - Kansas City (1987).

6. Calculations of Thermodynamic Properties of Alkali Halides and Sodium Nitrate. H. Yu, M.S. Thesis, University of Missouri - Kansas City (1987).

PRESENTATIONS

1. "Molecular Dynamics and Diffraction Studies of HAN." F. K. Ross, Liquid Propellant Meeting, BRL, August 1985.

2. "Monte Carlo Studies of Molten Salts." R. D. Murphy, Liquid Propellant Meeting, BRL, August 1985.

3. "Hydroxylammonium Nitrate: X-Ray Structure Determinations and the Use of Structure Information in Monte Carlo Calculations." F. K. Ross, T. B. Brill and R. D. Murphy, American Crystallographic Association, Stanford CA, August 1985.

4. "Neutron Diffraction Study of HAN Structure and Preliminary Liquid Scattering Measurements." F. K. Ross, Liquid Propellant Meeting, BRL, July 1986.

5. "Non-Spherical Electron Density Modeling from Single-Crystal X-ray and Neutron Diffraction Data." Q. Xie and F. K. Ross, American Physical Society, St. Louis MO, March 1989.

6. "Non-Spherical Electron Density Modeling from Single-Crystal X-ray and Neutron Diffraction Data." F. K. Ross, Q. Xie and E. O. Schlemper, American Crystallographic Association, Seattle WA (to be presented in July 1989).

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